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(54) Zinc alloys yielding anticorrosive coatings on ferrous materials

(57) ZINC ALLOY YIELDING ANTI-CORROSIVE COATINGS ON FERROUS MATERIALS, which includes zinc at a proportion of over 98%, aluminium, and at least one of the following alloy agents: chrome, nickel or vanadium. This alloy is used to obtain an anticorrosive coating on ferrous materials by means of hot-dip galvanizing, zinc spraying, etc..

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Description

OBJECT OF THE INVENTION

Zinc alloys yielding anticorrosive coatings on ferrous materials, consisting of zinc, aluminium, and at least one of the following alloy agents: nickel, vanadium, chrome.

HISTORY OF THE INVENTION

Corrosion is a frequent but undesirable process in certain metals. To avoid corrosion the metals are usually coated with a layer of zinc.

There are different methods known and used to coat steel and other metals with zinc and zinc alloys, such as: hot dip galvanizing, zinc spraying etc. One of the oldest methods still in use for economical and technical reasons is the so-called hot dip galvanizing process.

batch

Hot dip galvanizing basically consists of the immersion, for a few minutes, of ferrous materials in a molten zinc bath at a temperature of between 430ø and 560øC.

Hot dip immersion produces a physicochemical mechanism by which a diffusion process takes place between the base iron of the parts and the zinc.

The zinc coating gives the ferrous metals good corrosion resistance.

In general, a zinc coating obtained by hot dip galvanizing consists of several layers: an internal alloy of iron and zinc which adheres to the surface of the ferrous material, and an external layer, consisting almost entirely of pure zinc, according to the composition of the bath, called the Eta phase. In the interior layer, formed by the diffusion of zinc into the ferrous material, up to three zones or sub-layers can be distinguished, identified by their different iron contents. The sub-layer closest to the base material is called the Gamma phase and contains 21% to 28% iron. Next is the Delta phase, which contains from 6% to 11% iron, and finally the Zeta phase which contains approximately 6% iron.

Depending on the composition of the ferrous material of the part to be coated, the Zeta phase varies greatly in thickness and often tends to pass through to the external surface of the zinc. This occurs in steel used in the construction which has been taken as an example for this invention, the composition of which typically is:

- Carbon 0.06%- Manganese 0.33%
- Silicon 0.009%- Sulphur 0.010%
- Phosphorus 0.009%- Aluminium 0.028%
- Chrome 0.020%- Nickel 0.025%
- Copper 0.030%- Vanadium 0.006%
- Molybdenum 0.004%

When this construction grade steel is galvanized in a conventional zinc bath, without additional alloy agents, a galvanized coating with a relatively thin Delta phase and a Zeta layer are produced. The Zeta layer consists of large column crystals and reaches out to very near to the surface of the coating, while the Eta layer of pure zinc is almost non-existent.

The resulting coating layer has very low adherence because of the thick iron rich Zeta phase.

PURPOSE OF THE INVENTION

The invention consists of a zinc base alloy used to coat parts made of ferrous material. The invention offers a much finer Zeta layer, producing an improvement in its mechanical resistance, and a much thicker Eta phase, producing an important increase in the corrosion resistance of the coating.

Below, various alloys are described as examples of the present invention. The alloys contain zinc at a percentage equal to or over 98%, a percentage of aluminium equal to or lower than 0.25%, and the remainder, a percentage of up to 1.75%, is made up of one or more of the following metals: nickel, vanadium, chrome.

When the ferrous material is galvanized in a zinc alloy according to this invention, the coating structure is very different from that obtained when galvanized without said alloy. The Delta phase is very similar in appearance, but the Zeta layer, normally consisting of large column crystals, has been transformed into a relatively thin layer of crystals as a result of the inhibiting (levelling) action of the alloy agents, vanadium, nickel, chrome. A thick layer of zinc also appears (Eta phase) which, otherwise, is much thinner when galvanizing without said alloy agents. The new galvanized structure, with a relatively thin Delta and Zeta layers, increases the ductility and adherence of the coating, together with a greater resistance to corrosion, due to the greater thickness and compactness of the external layer of zinc, and also to the reduced fragility of the Zeta layer.

PRACTICAL EXAMPLES.

Steel construction parts, with composition as given above, were coated using the alloys described in the five examples below, where the concentrations are expressed as a percentage of weight. During the hot dip galvanizing process, the concentration of each alloy agent is kept between the given values.

Example 1.

The alloy subject to the invention is composed of aluminium at between 0.001% and 0.1%, vanadium at between 0.001% and 0.05%, and zinc making up the remainder.

Example 2

The alloy subject to the invention is composed of

aluminium at between 0.001% and 0.1%, nickel at between 0.002% and 0.1%, vanadium at between 0.001% and 0.05%, and zinc making up the remainder.

Example 3.

Cl 3 tempvalle !

The alloy subject to the invention is composed of vanadium at between 0.001% and 0.1%, chrome at between 0.05% and 0.5%, aluminium at between 0.001% and 0.2% and zinc making up the remainder.

Example 4.

The alloy subject to the invention is composed of chrome at between 0.005% and 0.5%, nickel at between 0.01% and 0.2%, aluminium at between 0.001% and 0.1%, and zinc making up the remainder.

Example 5.

The alloy subject to the invention is composed of vanadium at between 0.005% and 0.05%, nickel at between 0.005% and 0.1%, chrome at between 0.01% and 0.5%, aluminium at between 0.001% and 0.05%, and zinc making up the remainder.

In each of these examples a coating is obtained with improved mechanical and corrosion resistance characteristics as described below for example 2.

The coating's microstructure was examined under optical microscopy, using clear field and polarized light techniques on samples etched with nital at 2% (nitric acid at 2% in ethanol) and under scanning electron microscopy (SEM) on polished sections. The distribution and analysis of the elements was determined by X ray spectrometry (EDS) and glow discharge optical spectroscopy (GDOS). With the two techniques, EDS and GDOS, it was possible to observe that the alloy agents nickel and vanadium are sited mainly between the Delta and Zeta phases of the coating, restricting the growth of both intermetallic phases. This results in a more homogeneous coating with a thinner intermetallic layer, which provides great adherence and ductility, increasing the mechanical resistance of the coating. It also produces an external zinc layer which is thicker and more compact, thus greatly improving corrosion resistance.

To estimate the adherence of the coating, which reflects its mechanical resistance, the ASTM A-123 standard hammer test was used. The results of these tests show the strong adherence of the coatings obtained using the invention. The coating did not fracture between the two hammer blows, while the zinc coating without alloy agents fractured under the same conditions.

To compare the corrosion resistance of conventional galvanized coatings with those obtained using the protocols of the invention, accelerated corrosion tests were undertaken. The results are to be found in figure 1.

The graph shows the initial coating thickness required to resist corrosion in a salt-spray chamber, in accordance with the ASTM B-117-90 standard, for the time shown along the X-axis.

The parabolic curve represents the resistance values of a galvanized zinc product without alloy. The straight line represents the values given by a galvanized product using the alloy shown in example 2.

The graph shows that for the minimum thickness accepted as an industrial standard, 40 æm, the conventionally galvanized product resists for 400 hours, while the galvanized product with alloys, subject to the invention, resists corrosion for over 1300 hours. 70 æm of conventional galvanized product resists for some 600 hours, while a product coated in accordance with the invention resists corrosion for more than 2300 hours. With conventional galvanizing, increasing the coating to a thickness of over 140 æm does not improve resistance to more than 900 hours, while galvanizing with the alloy subject to the invention would make it possible to obtain corrosion resistance of over 2400 hours, with an increased thickness of slightly more than 70 æm.

With a minimum thickness of 40 æm, the invention offers a level of corrosion resistance which would need a thickness of much more than 160 æm if conventionally galvanized. This clearly shows that the invention not only improves the mechanical and corrosion resistances spectacularly, but also allows a saving in the consumption of zinc of more than 75%.

Having described in detail the nature of the invention, and having given practical examples of its use, it should be noted that modifications may be made thereto, as long as such do not represent a substantial change to the characteristics claimed below.

Claims

1. Zinc alloy yielding anti-corrosive coatings on ferrous materials; characterized as consisting of zinc plus its usual impurities, aluminium, and at least one of the following alloy agents: chrome, nickel, vanadium.

2. Alloy, according to claim 1, characterized by a zinc content of at least 98w/w%.

3. Alloy, according to claim 1, characterized by an aluminium content of between 0.001% and 0.25w/w%.

4. Alloy, according to claim 1, characterized by a nickel content of between zero and 0.6w/w%.

5. Alloy, according to claim 1, characterized by a vanadium content of between zero and 0.8w/w%.

6. Alloy, according to claim 1, characterized by a chrome content of between zero and 0.6w/w%.

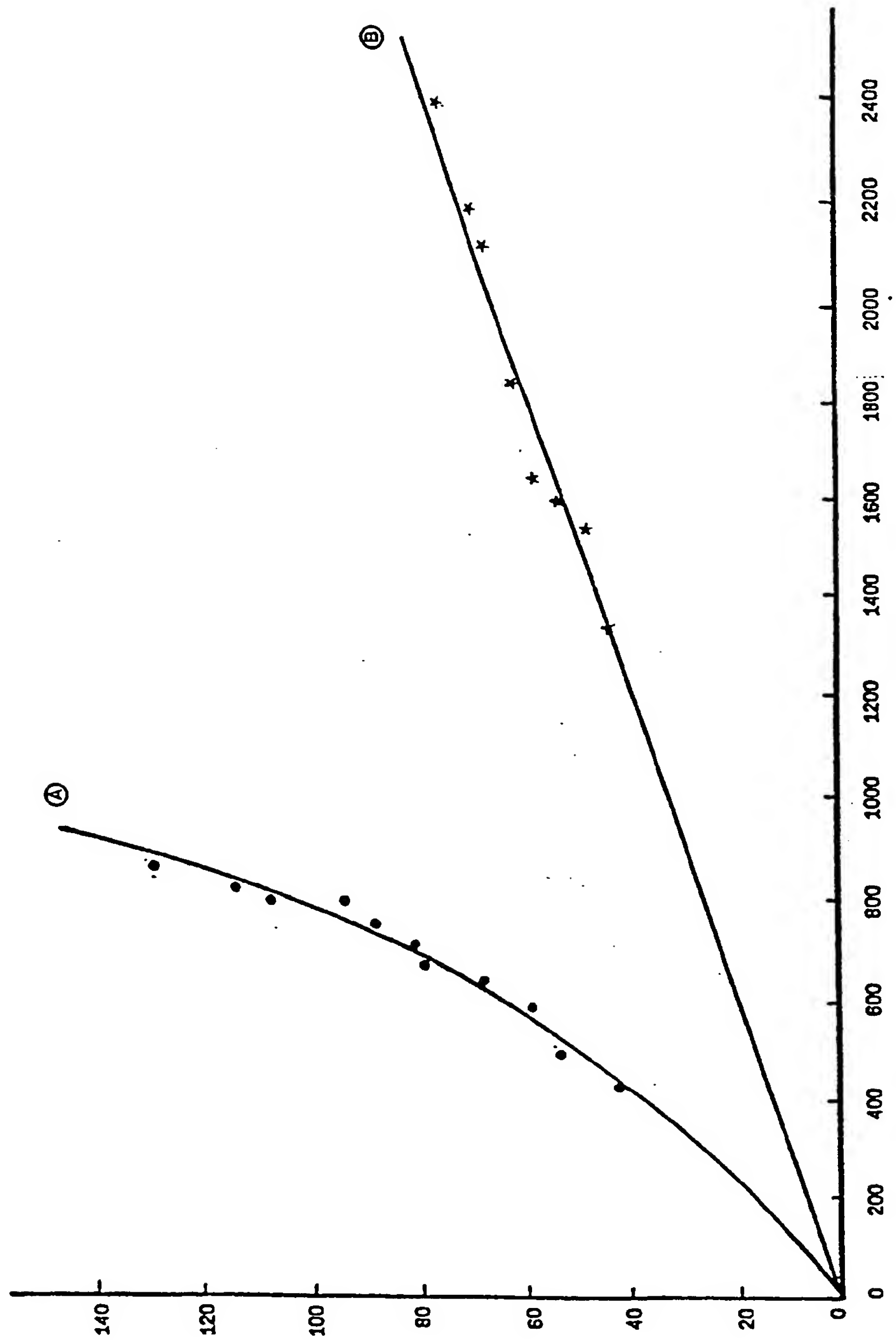
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Fig. 1

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EUROPEAN SEARCH REPORT

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EP 97 10 0008

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	PATENT ABSTRACTS OF JAPAN vol. 096, no. 007, 31 July 1996 & JP 08 060329 A (KOBE STEEL LTD) * Table, examples 1-3 * * abstract * ---	1-4	C22C18/04 C23C30/00
X	PATENT ABSTRACTS OF JAPAN vol. 018, no. 052 (C-1158), 27 January 1994 & JP 05 271892 A (NISSHIN STEEL CO LTD), 19 October 1993, * Table 1 * * abstract * ---	1-4	
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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
MUNICH	14 May 1997	Bjoerk, P

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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EUROPEAN SEARCH REPORT

Application Number
EP 97 10 0008

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
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The present search report has been drawn up for all claims

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MUNICH	14 May 1997	Bjoerk, P

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